

Singlet NMR in a Case of Exceptional Molecular Symmetry

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(Dated: June 21, 2025)

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I. SUPPLEMENTARY INFORMATION

A. Computational Chemistry

1. CSA Tensors

Estimates of the ^{13}C nuclear shielding tensors for the squarate dianion were obtained using the B3LYP functional using the ORCA¹ open source software package. The calculations do not take into account secondary isotope shifts. The shielding tensors for the four carbon sites are as follows:

$$\begin{aligned}\sigma_1 &= \begin{pmatrix} -86.787 & 0.457 & -0.552 \\ 0.478 & -112.518 & 0.23 \\ -0.468 & 0.22 & 66.533 \end{pmatrix} \text{ ppm}, \\ \sigma_2 &= \begin{pmatrix} -112.52 & -0.362 & -0.546 \\ -0.41 & -86.786 & 0.109 \\ -0.554 & 0.189 & 66.516 \end{pmatrix} \text{ ppm}, \\ \sigma_3 &= \begin{pmatrix} -86.740 & 0.451 & -0.402 \\ 0.435 & -112.491 & 0.233 \\ -0.493 & 0.220 & 66.523 \end{pmatrix} \text{ ppm}, \\ \sigma_4 &= \begin{pmatrix} -112.489 & -0.405 & -0.548 \\ -0.416 & -86.737 & 0.258 \\ -0.553 & 0.163 & 66.540 \end{pmatrix} \text{ ppm}.\end{aligned}\tag{1}$$

The calculated values of the isotropic parts of the shielding tensors are given as follows:

$$\sigma_1^{\text{iso}} = -44.258 \text{ ppm}, \quad (2)$$

$$\sigma_2^{\text{iso}} = -44.263 \text{ ppm}, \quad (3)$$

$$\sigma_3^{\text{iso}} = -44.236 \text{ ppm}, \quad (4)$$

$$\sigma_4^{\text{iso}} = -44.229 \text{ ppm}. \quad (5)$$

2. *J-Couplings*

The scalar couplings were estimated using the ORCA¹ open-source quantum chemistry package. Table SI reports the calculated values. The main text reports the average value of the *J*-couplings shown in the table below as the *J_{calc}* parameter.

Table SI. Keyword specifics used in computational calculations performed by ORCA¹, along with the different scalar coupling estimates for the 1,2-¹³C₂ and 1,3-¹³C₂-squarate molecules.

Keywords	¹ <i>J</i> ₁₂ /Hz	² <i>J</i> ₁₃ /Hz
B3LYP pcJ-3 TightSCF	56.31	47.35
B3LYP pcJ-3 VeryTightSCF	56.31	47.35
B3LYP pcJ-3 VeryTightSCF CPCM(water)	56.48	46.36
TPSSh pcJ-3 TightSCF	56.56	48.98
TPSSh pcJ-3 VeryTightSCF	56.56	48.98
TPSSh pcJ-3 VeryTightSCF CPCM(water)	56.68	47.97

B. Pulse Sequence Details

A singlet order filtration step is commonly used in singlet NMR experiments, in the form of a *T*₀₀ filter. This consists of a series of alternating pulsed field gradients and radio-frequency pulses that aim to dephase any operators that do not have the symmetry of the *T*₀₀

operator indicative of singlet order, thereby allowing only singlet operators to pass through. It can be written in the following form:

$$G_1 - 90^\circ_{\theta_m} - G_2 - 90^\circ_{\theta_m} - 90^\circ_{-x} - G_3, \quad (6)$$

where $\theta_m \approx \arctan \sqrt{2}$, or the magic-angle (54.7°).

A relaxation delay of $5 \times T_1$ was left between transients to allow the longitudinal magnetization to re-equilibrate. However, T_S values often exceed T_1 significantly, resulting in singlet order not having fully decayed by the next transient. The residual singlet order from previous transients may generate unwanted experimental artifacts. As a time-saving measure, we implemented a singlet order destruction (SOD) filter² at the start of the pulse sequence in our singlet-filtered experiments. This allowed the relaxation delay to be maintained at $5 \times T_1$, saving considerable amounts of experimental time.

The T_{00} and SOD filters' structures are depicted in Figure S1.

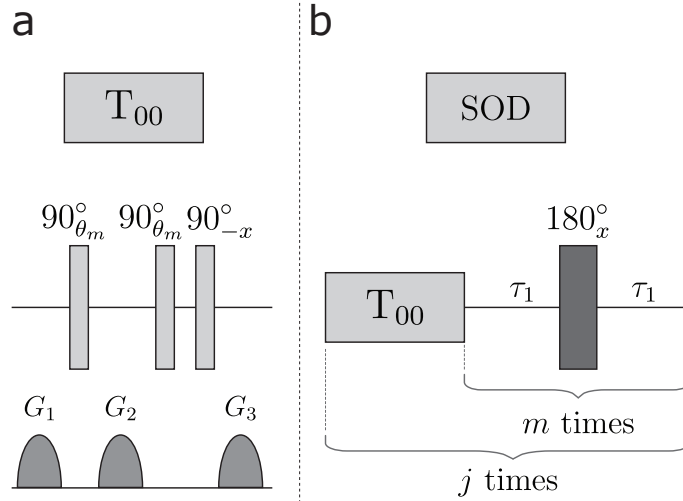


Figure S1. (a) Description of the T_{00} filter used in singlet NMR experiments, where the phase $\theta_m \approx 54.7^\circ$, the magic angle, and G_1 , G_2 and G_3 indicate field gradients. (b) Singlet order destruction² (SOD) filter, used to remove residual singlet order from the system. The parameters used in the experiments are given in the main text and Table SII. The darker colour indicates the implementation of a composite 180° pulse³.

The T_{00} and SOD filters' specific parameters are given in Table SII.

Table SII. T_{00} filter z -pulse gradient parameters used, and SOD filter loop number details.

T_{00}		
z -Gradient	Strength / %	Duration / ms
G_1	+15	4.4
G_2	-7.5	2.4
G_3	-7.5	2.0
SOD		
Parameter	1,2- $^{13}\text{C}_2$ -sq.	1,3- $^{13}\text{C}_2$ -sq.
m	14	10
j	4	4

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